References

ANDERSON, S. & WADSLEY, A. D. (1962). *Acta Cryst.* **15**, 201–206.

BANDO, Y., SEKIKAWA, Y., YAMAMURA, H. & MATSUI, Y. (1981). *Acta Cryst.* **A37**, 723–728.

BANDO, Y., WATANABE, M. & SEKIKAWA, Y. (1979). *Acta Cryst.* **B35**, 1541–1545.

BANDO, Y., WATANABE, M. & SEKIKAWA, Y. (1980). *J. Solid State Chem.* **33**, 412–419.

BANDO, Y., WATANABE, A., SEKIKAWA, Y., GOTO, M. & HORIUCHI, S. (1979). *Acta Cryst.* **A35**, 142–145.

BUXTON, B. F., EADES, J. A., STEEDS, J. W. & RACKHAM, G. M. (1976). *Philos. Trans. R. Soc. London Ser. A*, **281**, 171–194.

GOODMAN, P. (1975). *Acta Cryst.* **A31**, 804.

HORIUCHI, S., KIKUCHI, T. & GOTO, M. (1977). *Acta Cryst.* **A33**, 701–703.

MATSUI, Y., KATO, K., KIMIZUKA, N. & HORIUCHI, S. (1979). *Acta Cryst.* **B35**, 561–564.

TANAKA, M., SAITO, R. & WATANABE, D. (1980). *Acta Cryst.* **A36**, 350–352.

WATANABE, M., TSUTSUMI, M. & BANDO, Y. (1979). *J. Solid State Chem.* **28**, 397–399.

Special-Point Ordering in General Crystal Structures

BY J. M. SANCHEZ,* D. GRATIAS† AND D. DE FONTAINE

Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720, USA

Abstract

The classification of families of ordered structures, in terms of positions in reciprocal space where two or more symmetry elements of the pair potential intersect at a point, is extended to include general crystal structures. Only a relatively small number of space groups, 24 in all, are shown to be relevant to special-point ordering. The method is illustrated with the study of special-point families for a hexagonal crystal with two atoms per unit cell.

1. Introduction

General symmetry properties of pair potentials and of phenomenological free energies are, in many instances, sufficient to explain a wide range of phenomena related to order–disorder and/or magnetic phase transformations. The classical example of the power of such symmetry arguments is, undoubtedly, the well-known Landau theory of continuous phase transformations (Landau & Lifshitz, 1958). The concepts of symmetry,

* Present address: Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA.
† Permanent address: CECM/CNRS, 15 rue G. Urbain, 94400-Vitry, France.

and in particular that of 'special points' in reciprocal space – defined as points where two or more symmetry elements intersect – have been shown to be equally useful in the case of instabilities associated with other phase transitions (Khachaturyan, 1973; de Fontaine, 1975). It follows from symmetry considerations that at such special points scalar functions, endowed with the symmetry of the reciprocal lattice, will have, invariably, a minimum, a maximum or a saddle point. Thus, special points would seem to play an important role in, for example, the search for the lowest-energy (ground state) ordered structures (Clapp & Moss, 1968). It turns out, however, that special points are quite insufficient for a complete description of ground states which, in general, are more conveniently treated in real space (Kanamori & Kakehashi, 1977; Kudo & Katsura, 1976; Richards & Cahn, 1971; Allen & Cahn, 1972; Sanchez & de Fontaine, 1981).

Among the most important applications of special points is the study of the onset of short-wavelength instabilities in alloys (de Fontaine, 1975). Such instabilities may take place below a first-order transition, frequently bearing no symmetry relation to either the high- or low-temperature (equilibrium) phases (de Fontaine, 1981). This particular metastable ordering mechanism, known as spinodal ordering, has been observed, for example, by Okamoto & Thomas (1971)

in the NiMo system. The theory of special-point instabilities in f.c.c. and b.c.c. crystals and its application to the NiMo system has been developed by de Fontaine (1975). In a series of more recent publications, McConnell (1978a,b) has applied similar ideas to complex ordering in chalcopyrite and plagioclase feldspars.

The purpose of the present work is to explore the consequences of crystal symmetry on the pair potentials, for a general structure. As we shall see, the characterization of special points in a general structure, although straightforward, requires additional considerations usually not needed for crystals whose atoms are at the nodes of a Bravais lattice. We begin in § 2 by expressing the configurational energy in terms of normal concentration modes in reciprocal space. By formally establishing the point-group symmetry (that of the crystal plus inversion) and the translational symmetry (that of the reciprocal of the corresponding Bravais lattice) of the normal-mode energies, one obtains an associated space group consisting of all the symmetry elements of the pair potential. As we shall see, out of the 230 crystalline space groups, only 24 are relevant for special-point ordering. In § 4, the theory will be illustrated with the study of the instability families for the hexagonal structure with two atoms per unit cell ($P6_3/mmc$).

2. Configurational energy

Consider a general crystal structure with atomic species located at positions $\mathbf{r}_{mn} = \mathbf{R}_m + \mathbf{\rho}_n$, where $\mathbf{R}_m$ stands for a vector of the associated Bravais lattice and $\mathbf{\rho}_n$ is a vector within the primitive unit cell of the crystal. If we assume, for simplicity, that the crystal is composed of two different atomic species, the atomic configurations will be described by the spin operator $\sigma_n(\mathbf{R}_m)$, which takes values 1 or -1 depending on whether there is an A or B atom, respectively, at the position $\mathbf{r}_{mn}$.

In the pair approximation, the configurational energy takes the form:

$$E = \tfrac{1}{2} \sum_{nn'} \sum_{mm'} v_{nn'}(\mathbf{R}_m - \mathbf{R}_{m'}) \cdot \sigma_n(\mathbf{R}_m) \, \sigma_{n'}(\mathbf{R}_{m'}) \qquad (1)$$

where the matrix elements $v_{nn'}$ are given by:

$$v_{nn'}(\mathbf{R}_l) = v_{nn'}(\mathbf{R}_m - \mathbf{R}_{m'}) = v(\mathbf{R}_m + \mathbf{\rho}_n - \mathbf{R}_{m'} - \mathbf{\rho}_{n'}) \,(2)$$

with $v(\mathbf{r})$ an effective pair potential for rth neighbors. In terms of the interaction energies v^{AA}, v^{BB} and v^{AB} between the different atomic species, the effective interaction potential is given by:

$$v(\mathbf{r}) = \tfrac{1}{4}[v^{AA}(\mathbf{r}) + v^{BB} - 2v^{AB}(\mathbf{r})].$$

The configurational energy (equation 1) takes a simpler form when written in terms of reciprocal-space

variables. Assuming periodic boundary conditions for a sufficiently large region containing N Bravais lattice points, one can write the energy formula (equation 1) as:

$$E = \frac{N}{2} \sum_{\mathbf{k}} \sum_{nn'} V_{nn'}(\mathbf{k}) \, \sigma_n(\mathbf{k}) \, \sigma_{n'}(-\mathbf{k}) \qquad (3)$$

where the sum over the reciprocal vectors $\mathbf{k}$ runs over the first Brillouin zone of the reciprocal lattice, and where the Fourier-transformed spin operator and pair-interaction matrix $V_{nn'}$ are defined as follows:

$$\sigma_n(\mathbf{k}) = \frac{1}{N} \sum_m \sigma_n(\mathbf{R}_m) \exp(i\mathbf{k} \cdot \mathbf{R}_m) \qquad (4a)$$

and

$$V_{nn'}(\mathbf{k}) = \sum_l v_{nn'}(\mathbf{R}_l) \exp(-i\mathbf{k} \cdot \mathbf{R}_l)$$

$$= \sum_l v(\mathbf{R}_l + \mathbf{\rho}_n - \mathbf{\rho}_{n'}) \exp(-i\mathbf{k} \cdot \mathbf{R}_l) \quad (4b)$$

where the second equality in equation (4b) follows from equation (2). Note that the Fourier transform in equations (4a) and (4b) have been defined in such a manner that $\sigma_n(\mathbf{k})$ and $V_{nn'}(\mathbf{k})$ have the translational symmetry of the reciprocal lattice, which has been accomplished by choosing a different origin ($\mathbf{\rho}_n$) to calculate each of the $\sigma_n(\mathbf{k})$. If a common origin is chosen, the following alternate definition should be used:

$$\sigma'_n(\mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{\rho}_n) \, \sigma_n(\mathbf{k}) \qquad (5a)$$

$$V'_{nn'}(\mathbf{k}) = \exp[-i\mathbf{k} \cdot (\mathbf{\rho}_n - \mathbf{\rho}_{n'})] \, V_{nn'}(\mathbf{k}) \qquad (5b)$$

where $\mathbf{\rho}_n$ gives the position, with respect to the common origin, of the atom n.

The advantage of imposing translational symmetry on the interaction matrix $V_{nn'}(\mathbf{k})$ will become apparent in § 4, where the vanishing of certain elements of $V_{nn'}(\mathbf{k})$ will be inferred from symmetry arguments.

Equation (3) can be simplified further by diagonalizing the Hermitian matrix [see equation (13)] $V_{nn'}(\mathbf{k})$. Thus, the configurational energy becomes:

$$E = \frac{N}{2} \sum_{\mathbf{k}} \sum_n \omega_n(\mathbf{k}) \, \Gamma_n(\mathbf{k}) \, \Gamma_n(-\mathbf{k}) \qquad (6)$$

where ω_n are the eigenvalues of $V_{nn'}$ and Γ_n are the corresponding normal concentration modes.

Equation (6) has a form suitable for the instability analysis, namely that of a sum of an energy coefficient ω_n times a positive quantity $|\Gamma_n|^2$ characterizing the atomic distribution. Thus, in order to minimize the energy, the spectrum of the normal modes will tend to peak at those positions in reciprocal space where ω_n is minimum. As discussed in the Introduction, special points in reciprocal space are points where such minima of ω_n may, by symmetry, be present.

For the characterization of the special points, one must determine the space group G_ω which leaves the eigenvalues of the interaction matrix invariant. It will be seen in the next section that the space group in question is, in general, neither that of the crystal nor that of the reciprocal of the associated Bravais lattice.

3. Symmetry of the potential

Let G_x be the space group of the crystal. The symmetry elements of G_x are, in Seitz (1936) notation, $(\alpha_x|\tau)$ where α_x is a symmetry element of the point group of the crystal and τ is a translation (not necessarily a lattice translation). The operation $(\alpha_x|\tau)$ transforms any vector $\mathbf{r}$ in the crystal into an equivalent vector $\mathbf{r}'$ according to:

$$(\alpha_x|\tau)\,\mathbf{r} = \alpha_x\,\mathbf{r} + \tau = \mathbf{r}'.$$

The point-group symmetry operation α_x applied to the difference of two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ gives:

$$\alpha_x(\mathbf{r}_1 - \mathbf{r}_2) = \mathbf{r}_1' - \mathbf{r}_2' \qquad (7)$$

where $|\mathbf{r}_1 - \mathbf{r}_2| = |\mathbf{r}_1' - \mathbf{r}_2'|$. Since the effective potential $v(\mathbf{r})$ depends only on the distance between atoms, it will be invariant with respect to the symmetry operations of the point group of the crystal:

$$v(\mathbf{r}_1 - \mathbf{r}_2) = v[\alpha_x(\mathbf{r}_1 - \mathbf{r}_2)]. \qquad (8)$$

Likewise, the effective potential will be invariant with respect to the operation of inversion $(\bar{1})$:

$$v(\mathbf{r}_1 - \mathbf{r}_2) = v(\mathbf{r}_2 - \mathbf{r}_1). \qquad (9)$$

Thus, we conclude from equations (8) and (9) that the symmetry group G_v of the effective potential is the group generated by the union of the point-group symmetry elements of the crystal and the inversion center. The elements of G_v will be denoted by α_v:

$$v(\mathbf{r}) = v(\alpha_v\,\mathbf{r}). \qquad (10)$$

A point of interest for establishing the space group G_ω of the eigenvalues ω_n is the fact that G_v is always a subgroup of the point group of the Bravais lattice. Thus, if $\mathbf{R}_l$ is a lattice vector, we will have

$$\alpha_v\,\mathbf{R}_l = \mathbf{R}_{l'} \qquad (11)$$

with $\mathbf{R}_{l'}$ also a lattice vector.

Next, we obtain the transformation law for the elements of the interaction matrix at two points $\mathbf{k}$ and $\mathbf{k}'$ related by a symmetry operation of G_v, i.e. $\mathbf{k} = \alpha_v\,\mathbf{k}'$. By applying α_v to the argument of the real-space potential $v(\mathbf{r})$ in equation (4), and by using equations (10) and (11), we obtain the following expression for the element $V_{nn'}(\mathbf{k})$ of the interaction matrix:

$$V_{nn'}(\mathbf{k}) = \sum_l v[\alpha_v(\mathbf{R}_l + \boldsymbol{\rho}_n - \boldsymbol{\rho}_{n'})]\exp(-i\alpha_v\,\mathbf{k}.\alpha_v\,\mathbf{R}_l)$$

$$= \sum_{l'} v(\mathbf{R}_{l'} + \alpha_v\,\boldsymbol{\rho}_n - \alpha_v\,\boldsymbol{\rho}_{n'})\exp(-i\alpha_v\,\mathbf{k}.\mathbf{R}_{l'})$$

$$\qquad (12)$$

where we have explicitly used the following invariance property of the scalar product:

$$\mathbf{k}.\mathbf{R}_l = \alpha_v\,\mathbf{k}.\alpha_v\,\mathbf{R}_l = \alpha_v\,\mathbf{k}.\mathbf{R}_{l'}.$$

If α_v equals the inversion operation $\bar{1}$, which is not necessarily an element of the point group of the crystal, equation (12) reads:

$$V_{nn'}(\mathbf{k}) = \sum_{m'} v(\mathbf{R}_{l'} - \boldsymbol{\rho}_n + \boldsymbol{\rho}_{n'})\exp(+i\mathbf{k}.\mathbf{R}_{l'})$$

$$= V_{n'n}(-\mathbf{k}) \qquad (13)$$

stating simply that the matrix $V_{nn'}(\mathbf{k})$ is Hermitian. On the other hand, if α_v is a symmetry element of the point group of the crystal, we will have:

$$\alpha_v\,\boldsymbol{\rho}_n - \alpha_v\,\boldsymbol{\rho}_{n'} = \alpha_x\,\boldsymbol{\rho}_n - \alpha_x\,\boldsymbol{\rho}_{n'} = \mathbf{r} - \mathbf{r}',$$

where the vectors $\mathbf{r}$ and $\mathbf{r}'$ are, respectively, equivalent to $\boldsymbol{\rho}_n$ and $\boldsymbol{\rho}_{n'}$. Since, in general, $\mathbf{r}$ and $\mathbf{r}'$ will fall outside the unit cell of the crystal, we may introduce lattice translations $\mathbf{R}_\alpha^n$ and $\mathbf{R}_\alpha^{n'}$ such that:

$$\alpha_x\,\boldsymbol{\rho}_n - \alpha_x\,\boldsymbol{\rho}_{n'} = \boldsymbol{\rho}_{n_\alpha} - \boldsymbol{\rho}_{n_\alpha'} + \mathbf{R}_\alpha^n - \mathbf{R}_\alpha^{n'}, \qquad (14)$$

where $\boldsymbol{\rho}_{n_\alpha}$ and $\boldsymbol{\rho}_{n_\alpha'}$ are vectors within the unit cell. The index n_α generated by the symmetry operation α_x is such that the two vectors $\boldsymbol{\rho}_n$ and $\boldsymbol{\rho}_{n_\alpha}$ within the unit cell, although in general different, correspond to the same Wyckoff (1922) position. Thus, the net effect of the operation α_v on the set of vectors $\{\boldsymbol{\rho}_n\}$ is to generate a set of lattice translations, $\{\mathbf{R}_\alpha^n\}$, and a new set of transformed indices, $\{n_\alpha\}$, which is equal to a certain permutation of the original set $\{n\}$.

Combining equations (12) and (14), we obtain the following transformation rule for the element $V_{nn'}(\mathbf{k})$ of the pair-interaction matrix:

$$V_{nn'}(\mathbf{k}) = \exp(i\alpha_x\,\mathbf{k}.\mathbf{R}_\alpha^n)\,V_{n_\alpha n_\alpha'}(\alpha_x\,\mathbf{k})\exp(-i\alpha_x\,\mathbf{k}.\mathbf{R}_\alpha^{n'})$$

$$\qquad (15)$$

where the set $\{n_\alpha\}$ is, as explained above, a given permutation of the set $\{n\}$, and where the $\mathbf{R}_\alpha^n$ are lattice-translation vectors defined by equation (14).

It follows from equation (15) that the interaction matrices at position $\mathbf{k}$ and at position $\alpha_x\,\mathbf{k}$ are related by a similarity transformation of the form:

$$V(\mathbf{k}) = M^{-1}\,V(\alpha_x\,\mathbf{k})\,M \qquad (16)$$

where M is the product of a matrix S, which exchanges columns of V, times a diagonal matrix with elements $\exp(-i\alpha_x\,\mathbf{k}.\mathbf{R}_\alpha^n)$. Since two matrices related by a similarity transformation have the same eigenvalues,

we conclude that the normal-mode energies $\omega_n(\mathbf{k})$ are invariant to the symmetry operations α_ν:

$$\omega_n(\mathbf{k}) = \omega_n(\alpha_\nu \mathbf{k}). \qquad (17)$$

Furthermore, the ω_n have the translational symmetry of the reciprocal lattice:

$$\omega_n(\mathbf{k}) = \omega_n(\mathbf{k} + \mathbf{g}) \qquad (18)$$

where the reciprocal-lattice vectors $\mathbf{g}$ are such that $\mathbf{g}.\mathbf{R}_m = 2\pi L$ (L integer) for all vectors $\mathbf{R}_m$ of the Bravais lattice. Note, furthermore, that $\alpha_\nu \mathbf{g}$ is also a reciprocal-lattice vector:

$$\alpha_\nu \mathbf{g} = \mathbf{g}'. \qquad (19)$$

Thus, in the Seitz notation, the normal-mode energies ω_n are invariant to the symmetry operation $(\alpha_\nu|\mathbf{g})$. The associated space group G_ω is therefore [see equations (17), (18) and (19)] the direct product of G_ν, a centered group, times the translation group $\{\mathbf{g}\}$:

$$G_\omega = G_\nu \otimes \{\mathbf{g}\}.$$

We then arrive at the result that all relevant space groups G_ω for special-point instabilities are centered symmorphic groups, i.e. a center of inversion is always present and the generators of the group do not contain glide planes or screw axes.

The characterization of the special points associated to a given crystal structure can be summarized as follows. By introducing a center of inversion (if absent) into the symmetry class of the crystal G_x, we first determine the relevant point group G_ν. The next step consists in determining the reciprocal of the associated Bravais lattice, from which the translational symmetry of G_ω is obtained. Finally, the special points of interest are given by those Wyckoff positions of the centered-symmorphic group G_ω with fixed coordinates.

From the *International Tables for X-ray Crystallography* (1952) a list of all the 24 centered symmorphic groups, together with their special points, has been compiled in Table 1. Note that the special points listed in Table 1 are given with respect to the reciprocal-lattice coordinates.

4. Special-point families for hexagonal systems

As an application of the study of special points in general structures, we consider a hexagonal crystal with two atoms per unit cell ($P6_3/mmc$). The associated Bravais lattice and its reciprocal are both hexagonal. Thus, the translational symmetry of the normal-mode energies is that of the hexagonal lattice. The symmetry class of the crystal is $6/mmm$, which already contains a center of inversion, and, therefore, it coincides with the symmetry group G_ν of the real-space potential. Thus, according to our discussion in § 3, the special points of interest are those of the centered

symmorphic group obtained from the direct product of $6/mmm$ times the hexagonal translation group of the reciprocal lattice. The space group in question is $P6/mmm$, containing six special points (see Table 1).

Since there are two atoms per unit cell, at special positions 000 ($n = 1$) and $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ ($n = 2$), the pair-interaction matrix $V_{nn'}(\mathbf{k})$ is 2×2, with eigenvalues:

$$\omega_1(\mathbf{k}) = V_{11}(\mathbf{k}) - |V_{12}(\mathbf{k})| \qquad (20a)$$

and

$$\omega_2(\mathbf{k}) = V_{11}(\mathbf{k}) + |V_{12}(\mathbf{k})| \qquad (20b)$$

where $V_{11}(\mathbf{k})$ and $V_{12}(\mathbf{k})$ are given in terms of the real-space interaction energies by equation (4). Table 2 gives the values of ω_1 and ω_2 at the special points, for the case where up to four interaction energies $v(\mathbf{r})$ are

Table 1. *The 24 centered symorphic groups*

Special-point coordinates are given in terms of reciprocal-lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$.

System	Space groups (reciprocal space)	Special points
Triclinic	$P\bar{1}$	000; ½00; 0½0; 00½; ½½0; ½0½; 0½½; ½½½
Monoclinic	$P2/m$	000; ½00; 0½0; 00½; ½½0; ½0½; 0½½; ½½½
	$C2/m$ (2nd set)	000; 100; 00½; 10½; ½½0; ½½½
Orthorhombic	$Pmmm$	000; ½00; 0½0; 00½; ½½0; ½0½; 0½½; ½½½
	$Cmmm$	000; 100; 00½; 10½; ½½0; ½½½
	$Fmmm$	000; 001; 0½½; ½0½; ½½0; ½½½
	$Immm$	000; 100; 010; 001; ½½½
Tetragonal	$P4/m$ P/mmm	000; ½00; 00½; ½½0; ½0½; ½½½
	$I4/m$ $I4/mmm$	000; 100; 001; 10½; ½½½
Trigonal	$P\bar{3}$	000; ½00; 00½; ½0½
	$P\bar{3}1m$	000; ½00; 00½; ½0½; ⅓⅓0; ⅓⅓½
	$P\bar{3}m1$	000; ½00; 00½; ½0½
	$R\bar{3}$ $R\bar{3}m$	000; ½00; 00½; ½0½
Hexagonal	$P6/m$ $P6/mmm$	000; ½00; 00½; ½0½; ⅓⅓0; ⅓⅓½
Cubic	$Pm\bar{3}$ $Pm\bar{3}m$	000; ½00; ½½0; ½½½
	$Fm\bar{3}$ $Fm\bar{3}m$	000; 100; ½½0; ½½½
	$Im\bar{3}$	000; 100; ½½½
	$Im\bar{3}m$	000; 100; 1½0; ½½½

Table 2. *Normal-mode energies for the hexagonal system with four different interaction energies v_i, $i = 1, 2, 3, 4$ (see Fig. 1)*

Special point	$\omega_1(k)$	$\omega_2(k)$
000	$3v_1 + v_4 - 3|v_2'+ v_3|$	$3v_1 + v_4 + 3|v_2 + v_3|$
½00	$-v_1 + v_4 - |3v_3 - v_2|$	$-v_1 + v_4 + |3v_3 - v_2|$
00½	$3v_1 - v_4$	$3v_1 - v_4$
½0½	$-v_1 - v_4$	$-v_1 - v_4$
⅓⅓0	$-\tfrac{3}{2}v_1 + v_4$	$-\tfrac{3}{2}v_1 + v_4$
⅓⅓½	$-\tfrac{3}{2}v_1 - v_4$	$-\tfrac{3}{2}v_1 - v_4$

considered. The interaction energies in question [$v_i \equiv v(r_i)$, $i = 1, 2, 3, 4$] are indicated in Fig. 1. The regions in the interaction-parameter space within which the normal-mode energy for a given special point is minimum are shown in Fig. 2 for the special case $v_3 = v_4 = 0$. Similar plots are shown in Fig. 3 where the ordinate and the abscissa are, respectively, the ratios $\alpha_3 = v_4/v_1$ and $\alpha_2 = v_2/v_1$.

Note that, at the special points $00\frac{1}{2}$; $\frac{1}{3}\frac{1}{3}0$; $\frac{1}{3}\frac{1}{3}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$, the off-diagonal element $V_{12}(\mathbf{k})$ of the interaction matrix vanishes, making the two normal concentration modes degenerate in energy. Such degeneracies are not accidental, and they can be easily explained by means of the transformation rule, equation (15), for the interaction matrix. In fact, if α_x in equation (15) is taken to be the mirror plane through the origin and perpendicular to the sixfold axis, we obtain $n_\alpha = n$ (for $n = 1, 2$), $\mathbf{R}_\alpha^1 = 000$ and $\mathbf{R}_\alpha^2 = 001$. Thus, for $V_{12}(\mathbf{k})$, equation (15) yields:

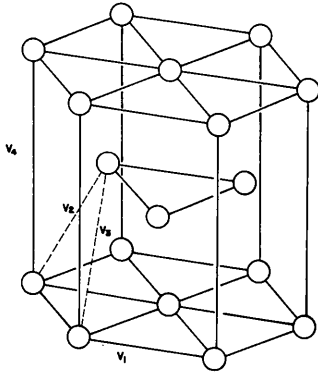$$V_{12}(\mathbf{k}) = V_{12}(\mathbf{k}') \exp(i\varphi) \qquad (21)$$

Fig. 1. The hexagonal crystal structure. The four interaction parameters used in normal-mode energy calculations are indicated (v_i, $i = 1, 2, 3, 4$).
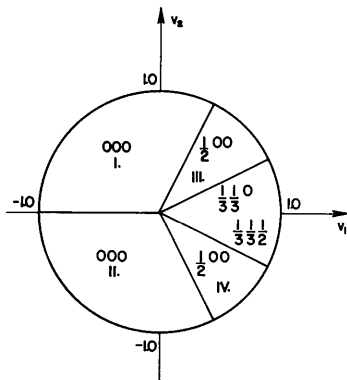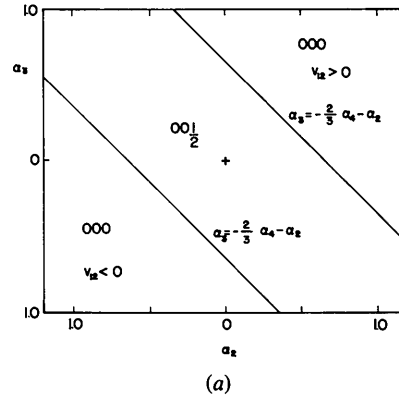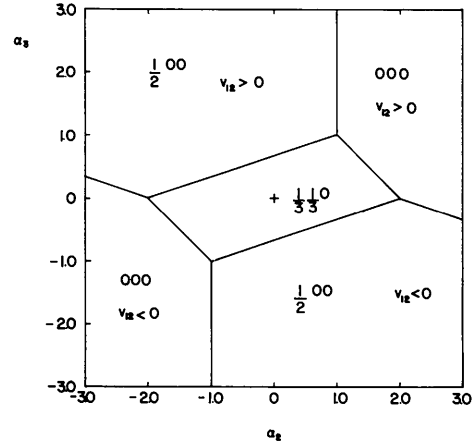

Fig. 2. Regions of minimum value of normal-mode energies for nearest-neighbor interactions on the basal plane (v_1) and between adjacent basal planes (v_2). Regions I and II for special point 000 correspond, respectively, to ordering (see Fig. 4a) and clustering. Representative structures for subfamilies III and IV of special point $\frac{1}{2}00$ are shown, respectively, in Fig. 4(b) and (c). Special-point families $\frac{1}{3}\frac{1}{3}0$ and $\frac{1}{3}\frac{1}{3}\frac{1}{2}$ are degenerate in energy.

where $\mathbf{k}'$ is related to $\mathbf{k}$ through the mirror in question, and where $\varphi = \mathbf{k}' \cdot \mathbf{R}_\alpha^2$. If we now choose $\mathbf{k}$ equal to the special point $00\frac{1}{2}$, equation (21) becomes:

$$V_{12}(00\tfrac{1}{2}) = -V_{12}(00\tfrac{1}{2})$$

(a)

(b)
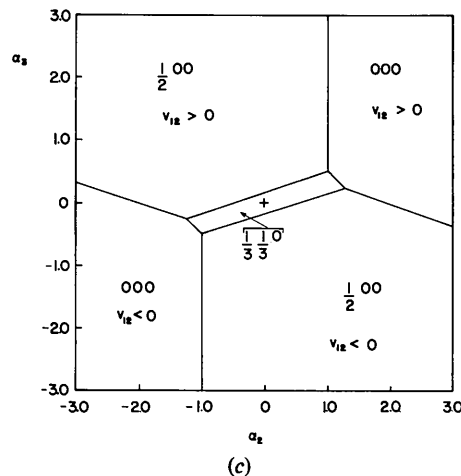
(c)

Fig. 3. Regions of minimum value of normal-mode energies for hexagonal system with four pair interactions (see Fig. 1). Ordinate and abscissa are, respectively, the ratios $\alpha_3 = v_3/v_1$ and $\alpha_2 = v_2/v_1$. Different plots correspond to (a) $v_1 < 0$, $\alpha_4 = v_4/v_1 = 1\cdot0$; ($b$) $v_1 > 0$, $\alpha_4 = 1\cdot0$; (c) $v_1 > 0$, $\alpha_4 \leq 0$.

which implies the vanishing of $V_{12}(00\frac{1}{2})$ since $V_{nn'}(\mathbf{k})$ has the translational symmetry of the reciprocal lattice and since, furthermore, the vectors $00\frac{1}{2}$ and $00\bar{\frac{1}{2}}$ are related by $\mathbf{g} = 001$. Equation (15) can be similarly applied to other special points and symmetry elements: the mirror plane perpendicular to the sixfold axis also implies the vanishing of $V_{12}(\mathbf{k})$ at $\frac{1}{2}0\frac{1}{2}$ and at $\frac{1}{3}\frac{1}{3}\frac{1}{2}$, whereas the threefold axis requires V_{12} to vanish at $\frac{1}{3}\frac{1}{3}0$. In general, a given symmetry element α will require the vanishing of certain elements of the interaction matrix at a position $\mathbf{k}$ in reciprocal space, if: (i) $\alpha\mathbf{k} = \mathbf{k} + \mathbf{g}$; i.e. $\mathbf{k}$ is on the Brillouin-zone boundary [the case $\mathbf{k} = \mathbf{g}$ is excluded, see rule (iii)]; (ii) the permutation connecting the set $\{n_\alpha\}$ to $\{n\}$ is the identity; and (iii) the phase shift is such that $\mathbf{k}.(\mathbf{R}^n_\alpha - \mathbf{R}^{n'}_\alpha) \neq 2\pi L$ with L integer.

4(a). Non-degenerate special points

For the case of the hexagonal lattice with two atoms per unit cell, the Fourier transforms of the spin operators at non-degenerate special points are given by:

$$\sigma_1(\mathbf{k}) = \frac{1}{\sqrt{2}} [\Gamma_1(\mathbf{k}) + \Gamma_2(\mathbf{k})]$$

$$\sigma_2(\mathbf{k}) = \frac{1}{\sqrt{2}} [-\Gamma_1(\mathbf{k}) + \Gamma_2(\mathbf{k})] \exp[-i\theta(\mathbf{k})]$$

where $\Gamma_i(\mathbf{k})$ are the normal-mode amplitudes [see equation (6)] and where $\theta(\mathbf{k})$ is defined by:

$$V_{12}(\mathbf{k}) = |V_{12}(\mathbf{k})| \exp[i\theta(\mathbf{k})]. \tag{22}$$

It follows from equation (20), that ω_2 is always larger than ω_1. Thus, the lowest-energy state corresponds to $\Gamma_2(\mathbf{k}) = 0$, in which case

$$\sigma_1(\mathbf{k}) = \frac{1}{\sqrt{2}} \Gamma_1(\mathbf{k})$$

and

$$\sigma_2(\mathbf{k}) = -\sigma_1(\mathbf{k}) \exp[-i\theta(\mathbf{k})]. \tag{23}$$

Since $\theta(\mathbf{k})$ will in general depend on the choice of unit cell, it is more convenient to express equation (23) in terms of the unit-cell-independent phase factor $\theta'(\mathbf{k})$ defined as follows:

$$V'_{12}(\mathbf{k}) = |V'_{12}(\mathbf{k})| \exp[i\theta'(\mathbf{k})]$$

where $V'_{12}(\mathbf{k})$ is given by equation (5b). Thus, combining equations (5b), (22) and (23), we obtain:

$$\sigma_2(\mathbf{k}) = -\sigma_1(\mathbf{k}) \exp[-i\theta'(\mathbf{k})].\exp[-i\mathbf{k}.(\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2)]$$

where $\boldsymbol{\rho}_1$ and $\boldsymbol{\rho}_2$ are vectors giving the positions of the two atoms in the unit cell. There are two non-degenerate special-point families in the hexagonal lattice, namely those corresponding to special points 000 and $\frac{1}{2}00$. Each of the families splits into two

subfamilies, depending on the sign of V_{12} [V_{12} is real at 000 and $\frac{1}{2}00$, as can easily be seen from its definition, equation (4)]. The families in question correspond to $\sigma_2(\mathbf{k}) = -\sigma_1(\mathbf{k})$ for $\theta(\mathbf{k}) = 0$ (i.e. $V_{12} > 0$) and $\sigma_2(\mathbf{k}) = \sigma_1(\mathbf{k})$ for $\theta(\mathbf{k}) = \pi$ (i.e. $V_{12} < 0$). The representative structures of the 000 family are pure A (or B) for $V_{12} < 0$ (i.e. clustering) and an ordered structure consisting of an alternate sequence of pure A, pure B, pure A...basal planes for $V_{12} > 0$. A unit cell for the latter structure (space group $P\bar{6}m2$) is shown in Fig. 4(a), where open and full circles correspond to the two atomic species, and where atoms on adjacent basal planes are represented by circles of different sizes.

For the $\frac{1}{2}00$ family, two ordered subfamilies result. Their representative structure, both of stoichiometry AB, are shown in Fig. 4(b) (space group $Pmma$) for $V_{12} < 0$ and in Fig. 4(c) (space group $Pmmn$) for $V_{12} \geq 0$. The structure shown in Fig. 4(b) is that of the MgCd system and it has been found by Kudo & Katsura (1976), together with the structures shown in Fig. 4(a) and (c), to be the ground state of the h.c.p. lattice with first- and second-neighbor pair interactions.
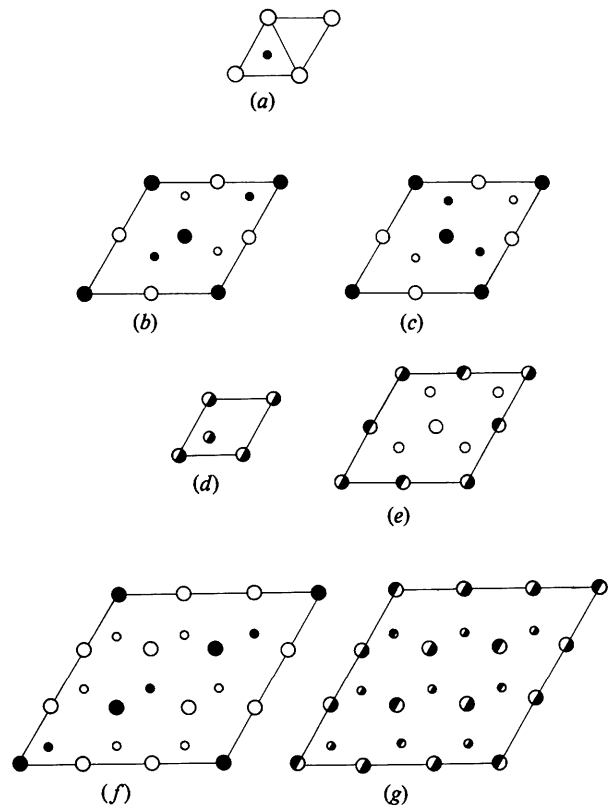

Fig. 4. Representative structures for each of the special-point families: (a) 000 ($P\bar{6}m2$); (b) $\frac{1}{2}00$ ($Pmma$); (c) $\frac{1}{2}00$ ($Pmmn$); (d) $00\frac{1}{2}$ ($P\bar{3}m1$); (e) $\frac{1}{2}0\frac{1}{2}$ ($C2/m$); (f) $\frac{1}{3}\frac{1}{3}0$ plus 000 ($Cmcm$) and (g) $\frac{1}{3}\frac{1}{3}\frac{1}{2}$ plus $00\frac{1}{2}$ ($C2/m$).

4(b). Degenerate special points

For degenerate special ponts, the Fourier transforms of the spin operators are equal to the normal-mode amplitudes. The representative structures of stoichiometry AB for the $00\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$ special points are shown, respectively, in Fig. 4(d) (space group $P\bar{3}m1$) and Fig. 4(e) (space group $C2/m$) where half-shaded circles indicate that the two atomic species alternate along the [001] direction. Since the structures corresponding to the special points $00\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$ require at least fourth-neighbor interactions to be stable, they have not been reported by Kudo & Katsura (1976), who included up to third-neighbor interactions in their analysis of the h.c.p. system.

The remaining degenerate special points, namely $\frac{1}{3}\frac{1}{3}0$ and $\frac{1}{3}\frac{1}{3}\frac{1}{2}$, are such that, by themselves, they do not give rise to a perfect ordered structure. To obtain a structure with these special points, one must at least include one additional concentration plane wave in the Fourier spectrum of the spin operators $\sigma_n(R)$. Fig. 4(f) shows a structure of stoichiometry A_2B, found to be a ground state by Kudo & Katsura (1976), obtained with special points $\frac{1}{3}\frac{1}{3}0$ and 000 (space group $Cmcm$). The special point $\frac{1}{3}\frac{1}{3}\frac{1}{2}$ together with $00\frac{1}{2}$ give rise to the structure of stoichiometry AB (space group $C2/m$) shown in Fig. 4(g).

The failure of certain special points to give rise to an ordered structure and, conversely, the fact that many real ordered structures contain points which are not special points, clearly indicates that the analysis presented here does not properly apply to the study of ground-state structures. Nevertheless, as mentioned in the *Introduction*, the classification of ordered structures into special-point families becomes significant when instabilities are studied.

5. Conclusion

The highest instability temperature, defined as the temperature at which the disordered solid solution first becomes unstable, can be shown to occur for concentration waves with wave vectors located at the absolute minimum of the Fourier transform of the pair potentials (de Fontaine, 1975). Thus, the relevance of special points to the study of ordering instabilities in solid solutions rests on the symmetry requirement that, at such points, the pair potential must have a minimum, a maximum or a saddle point.

It would appear at first that a classification of systems in terms of special points would be overly restrictive since, in principle, instabilities may occur for any position k in reciprocal space. However, special-point ordered structures have the smallest Bravais lattice compatible with the high-temperature disordered phase and, thus, will invariably be ground states for short-range-interaction potentials. For metal-

lic systems, in particular, the real-space pair potential decays relatively fast with the interatomic distance and therefore most solid solutions will in fact be expected to display only special-point instabilities.

In the disordered state, such systems will be characterized by large-amplitude fluctuations of the special-point concentration wave. Thus the short-range-order intensity, as measured for example in X-ray scattering experiments, will be maximum at certain special-point positions. The instability itself will in general take place below an equilibrium phase transition and, thus, will only be brought into play by fast quenching of the solid solution. Such a non-equilibrium spinodal ordering mechanism is best observed when the unstable concentration wave is not part of the concentration spectrum of the equilibrium phase, as in the case of the NiMo system studied by Okamoto & Thomas (1971).

The classification in terms of special-point families should prove to be particularly useful in the case of complex ordering in minerals and low-symmetry structures in general, where a complete ground-state analysis cannot be carried out as readily as in the f.c.c. or b.c.c. crystal structures. Unlike the case of crystals with one atom per unit cell, where the special points relevant to ordering are those of the associated reciprocal lattice, we have found that in general structures such points are not necessarily those of the reciprocal of the Bravais lattice. A convenient way of analyzing such general structures is to introduce an interaction matrix and its associated normal concentration modes. The special points of interest are those of the space group of the eigenvalues of the interaction matrix, *i.e.* the energies of the normal concentration modes. The space groups in question are found to be centered symmorphic groups, 24 in all, obtained from the direct product of the symmetry class of the crystal plus inversion, times the translation group of the reciprocal of the associated Bravais lattice. Our results concerning the symmetry of the normal-mode energies in reciprocal space, follow directly from the transformation rule for the interaction matrix [see equation (15)]. An important application of equation (15) concerns the study of special-point degeneracies, as was shown in § 4 for the hexagonal system. Such degeneracies are related to symmetry elements of the associated centered-symmorphic space group and they can be studied, by means of equation (15), without referring to the particular atomic distribution in real space.

References

ALLEN, S. M. & CAHN, J. W. (1972). *Acta Metall.* **20**, 423–433.

CLAPP, P. C. & MOSS, S. C. (1968). *Phys. Rev.* **171**, 754–763.

FONTAINE, D. DE (1975). *Acta Metall.* **23**, 533–571.

FONTAINE, D. DE (1981). *Metall. Trans. A*, **12A**, 559–566.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

KANAMORI, J. & KAKEHASHI, Y. (1977). *J. Phys. (Paris)*, **38**, C7274–C7279.

KHACHATURYAN, A. G. (1973). *Phys. Status Solidi*, **60**, 9–37.

KUDO, T. & KATSURA, S. (1976). *Prog. Theor. Phys.* **56**, 435–449.

LANDAU, L. D. & LIFSHITZ, E. M. (1958). *Statistical Physics*, p. 386, Reading, Mass.: Addison-Wesley.

MCCONNELL, J. D. C. (1978a). *Phys. Chem. Miner.* **2**, 253–265.

MCCONNELL, J. D. C. (1978b). *Z. Kristallogr.* **147**, 45–62.

OKAMOTO, P. R. & THOMAS, G. (1971). *Acta Metall.* **19**, 825–841.

RICHARDS, M. J. & CAHN, J. W. (1971). *Acta Metall.* **19**, 1263–1277.

SANCHEZ, J. M. & DE FONTAINE, D. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'KEEFFE & A. NAVROTSKY. New York: Academic Press. In the press.

SEITZ, F. (1936). *Ann. Math.* **37**, 17–26.

WYCKOFF, R. W. G. (1922). *The Analytical Expression of the Results of the Theory of Space Groups*. The Carnegie Institution, Washington, DC.

The Subgroups of the Finite Double Point Groups

BY WALDEMAR GORZKOWSKI*

Universität Duisburg, Fachbereich 10, Theoretische Physik, Duisburg, Federal Republic of Germany

Abstract

Theorems referring to subgroups of the finite double point groups are formulated. All possible non-evident subgroups are enumerated. The results obtained for subgroups correspond to well known Opechowski rules for classes of double groups.

For some purposes, *e.g.* for finding the transitive permutational representations (Hall, 1959; Gorzkowski, 1976) playing a very important role in so-called coloured symmetry, it is necessary to know all the subgroups of the finite double point groups. This problem is analyzed in this paper. Three theorems referring to the subgroups of the finite double point groups will be formulated. In a certain sense these theorems are analogous to the well known Opechowski (1940) rules referring to the classes of double point groups.

According to Gorzkowski & Suffczynski (1978) we remark that if H is a subgroup of the single group G, then the double group $\bar{H}$ is a subgroup of the double group $\bar{G}$. This fact is used implicitly in many expositions dealing with the double groups (*e.g.* Bradley & Cracknell, 1972) and it will not be proved here.

* Permanent address: Instytut Fizyki PAN, al. Lotnikow 32/46, 02-668 Warszawa, Poland.

A subgroup of the double point group which itself is a double group in the sense that it includes the identity E and the rotation $\bar{E}$ through the angle 2π shall be called an evident subgroup. The problem of the non-evident subgroups of all the crystallographic double point groups has been solved (Gorzkowski & Suffczynski, 1978). Now the finite double point groups without crystallographic restrictions are investigated.

At the beginning, for simplicity, the double point groups without improper rotations are taken into account. The following theorem will be proved.

Theorem 1

Every non-evident subgroup of the finite double point group without improper rotations can contain only the rotations $C^l_{n+\frac{1}{2}}$ through the angles $4\pi l/(2n + 1)$ where l and n are integers.

Proof. At first the even-order symmetry axis is considered. Let C_{2n} denote the rotation through the angle $2\pi/2n = \pi/n$, and $\bar{C}_{2n}$ the rotation through the angle $\pi/n + 2\pi$. One can have:

$$C^{2n}_{2n} = \bar{C}^{2n}_{2n} = \bar{E}.$$

We see that the group generated by C_{2n} or $\bar{C}_{2n}$ contains both $\bar{E}$ and E. Therefore, the subgroup containing the even-order symmetry axis is an evident one.

Now the odd-order symmetry axis is taken into account. Let C_{2n+1} denote the rotation through the